

Vibrational anharmonicity and Debye-Waller factors of fcc metals

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An application of Willis anharmonic approach has been made to improve authors' previous calculations of the Debye-Waller factors of face-centred-cubic metals. The effect of including anharmonic terms in the crystal potential has been estimated. Results obtained compare very well with the experimental data in terms of the Debye-Waller factor temperature parameter.

1. INTRODUCTION

Results of calculation for the Debye-Waller factors of metals by Chandra *et al* (1975) agreed satisfactorily with the experimental observations only upto a certain temperature and thereafter theoretical values were found to be higher than experimental results. The most likely reason for this appeared to be the neglect of anharmonic effects significant at higher temperatures as dictated by Krivoglaz & Teklonova (1961), Hahn & Ludwig (1961), Maradudin & Plinn (1963), Cowley (1963), Kashwase (1965) and Willis (1969). Willis has attempted to remove this difficulty by assuming the Einstein model for anharmonic thermal motion of atoms in crystal and extended the anharmonic analysis to crystals with various structures. The theory has further been applied by Prakash *et al* (1973) to investigate the effect of lattice anharmonicity on the Debye-Waller factors of metals and has been found to show good agreement with experiments.

In the present paper, we have followed the Willis approach, which is quite rigorous and simple from the computation point of view, and have studied the anharmonic vibrational effects on the Debye-Waller factors for face centred cubic metals copper, silver, aluminium and nickel.

2. THEORY

The effect of thermal motion on the Bragg intensity is equivalent to multiplying the scattering amplitude of each atom l by the temperature factor (exponent of the Debye-Waller factor $W(Q)$), defined by

$$T(Q) = \exp[-W(Q)] = \langle \exp[iQu(l)] \rangle$$

Here $u(l)$ is the displacement of the l th atom from its equilibrium position and Q is the scattering vector ($Q = 4\pi \sin \theta/\lambda$).

The explicit temperature dependence of the temperature factor following the theoretical treatments of Willis as published in the paper of Prakash *et al* (1973) gives

$$T(Q) = \exp \left[-\frac{K_B T}{2\alpha_0} (1 + 2\chi\gamma_0 T) \left(1 - 20K_B T \frac{\gamma_0}{\alpha_0^2} \right) Q^2 \right],$$

or,

$$B(T) = B^h(T) \left[1 + T \left(2\chi\gamma_0 - 20K_B \frac{\gamma_0}{\alpha_0^2} \right) \right] \quad \dots (1)$$

where χ is the volume expansion coefficient, γ_0 the Gruneisen constant and α_0 , γ_0 are temperature independent potential parameters. $B(T)$ is the isotropic B -factor at temperature T , defined by

$$T(Q) = \exp \left[-B(T) \frac{\sin^2 \theta}{\lambda^2} \right]$$

and $B^h(T)$ is the harmonic B -factor at temperature T , given by

$$B^h(T) = 8\pi^2 k_B T / \alpha_0 \quad \dots (2)$$

Thus in the harmonic approximation B -values are proportional to temperature, whereas in the anharmonic crystal an extra term appears in the expression, which is proportional to the square of temperature. This term consists of two parts—one due to thermal expansion and the other due to quartic modification of the potential and representing the softening of the vibration at large amplitudes.

3 COMPARISON WITH EXPERIMENTS

A comparison between the computed results and the experimental values is made in terms of temperature parameter Y given by

$$(\lambda/\sin \theta)^2 \log_{10}(I_T/I_0) = Y = 0.43(\lambda/\sin \theta)^2 (2W_{T_0} - 2W_T) \quad \dots (3)$$

where I_T and I_{T_0} are the measured integrated intensities of a certain diffraction line at temperature T and T_0 .

The computed values for copper, silver, aluminium and nickel along with the experimental values are compared in figures 1 to 4. Curves *A* correspond to the harmonic theory based on our previous calculations of Debye-Waller factor using the extended de Launay model given by Shukla & Cavallero (1973). Curves *B* were obtained after applying quasi-harmonic corrections to $B^h(T)$ by retaining the thermal expansion term but writing $\gamma_0/\alpha_0^2 = 0$ in eq. (1). Curves *C* present eq. (3) with the anharmonic form of eq. (1) and were drawn by choosing γ_0/α_0^2 in such a way as to make the anharmonic curves pass through the experi-

mental points at the highest temperatures, where anharmonicity is the greatest. The harmonic value of parameter is obtained from relation (3)

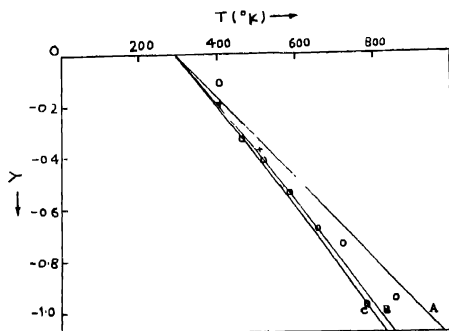


Fig. 1. Temperature variation of Y for copper. Curve A obtained from harmonic; B from quasi-harmonic and C from anharmonic calculations. Experimental points: + Flinn *et al*, O Owen & Williams.

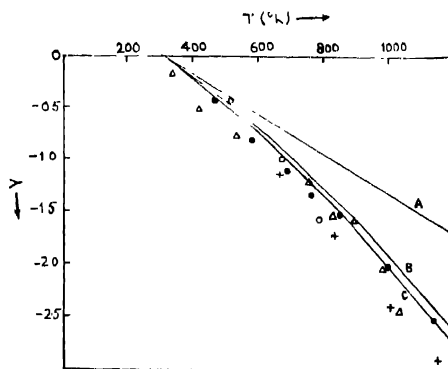


Fig. 2. Temperature variation of Y for silver. Curve A obtained from harmonic; B from quasi-harmonic and C from anharmonic calculations. Experimental points: O Boskovits *et al*; + Spreadborough & Christian; O Haworth; Δ Simerská.

Copper: Temperature variation measurements of the Debye-Waller factor from X-ray intensity have been made by Flinn *et al* (1961), Owen & Williams (1947). Former authors have made the observations over the temperature range 4.2 to 500°K while the later have covered the range from room temperature

293 to 851°K. We have chosen the experimental data of Owen & Williams for the present comparison. These are plotted in figure 1. The anharmonic curve *C* was allowed to pass through the experimental point at 785°K as this gives the best fit. The agreement of the calculated values of *Y* with experiments is fairly good.

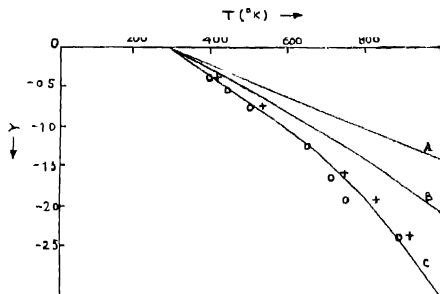


Fig. 3. Temperature variation of *Y* for aluminum. Curve A obtained from harmonic; B from quasi-harmonic and C from anharmonic calculations. Experimental points: + Owen & Williams; O Chipman.

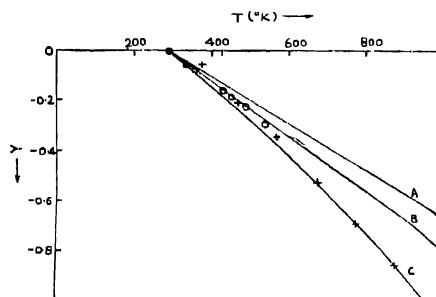


Fig. 4. Temperature variation of *Y* for nickel. Curve A obtained from harmonic; B from quasi-harmonic and C from anharmonic calculations. Experimental points: + Simerska, O Wilson *et al.*

Silver: Measurements of the temperature dependence of the Debye-Waller factors of silver have been made through X-ray diffraction techniques by Boskovits *et al* (1958), Spreadborough & Christian (1959), Haworth (1960) and Smerska (1961). The measurements of Haworth extend from room temperature (286°K)

to 1125°K and can be considered most exhaustive and reliable. For comparison, we have plotted the values of Y deduced from all the workers in figure 2. The anharmonic curve C was allowed to pass through the experimental points at $T = 1125^\circ\text{K}$. The calculated values show a reasonably satisfactory agreement with the experimental values of all.

Aluminium: Experimental study of the Debye-Waller factor for aluminium by X-ray determination has been made by James *et al* (1929), Owen & Williams (1947), Chipman (1960). We have chosen the data of Owen & Williams and Chipman for the present comparison. These are plotted in figure 3 along with the theoretical values of Y obtained by passing the anharmonic curve C through the experimental point at 865°K. Theoretical results agree satisfactorily with the experimental values.

Nickel: Experimental study of temperature variation of the X-ray Debye-characteristic temperature of nickel has been reported by Simerskå (1962) and Wilson *et al* (1966). Simerskå has taken the observation from room temperature (293°K) to 873°K, while Wilson *et al* have made over the range 100–520°K and correlated the data for thermal diffuse scattering and change of lattice parameter. The two measurements compare favourably throughout the range of their measurements. These are plotted in figure 4. The anharmonic curve was allowed to pass the experimental point at 873°K as this gives the best fit. The calculated values agree reasonably well with the experiments.

4. DISCUSSION

Our results show that temperature parameter Y obtained from the Willis approach for face-centred cubic metals copper, silver, aluminium and nickel provides a reasonable description of the observed temperature variation of the intensities of X-ray reflections. The order of accuracy of Y delivered from the experimental data of various workers varies from 3 to 8% in different cases of measurement as described in their papers.

In the case of copper and silver thermal expansion accounts for the bulk of the anharmonic contribution to the Debye-Waller factor. However, there is small quartic contribution represented by the difference between curve B and C . While in case of aluminium and nickel anharmonicity is considerable. Conclusively anharmonic effects are accounted satisfactorily by using the Einstein model approach. However it requires more precise experimental data for its critical appraisal.

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